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Stabilization of Colouring Compositions Containing Diazonium Salts

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This invention relates to compositions containing ice colour diazo components, diazotized or undiazotized and to methods of preventing the thinning of printing pastes containing such diazo components.

Producing prints of ice colours on various vegetable fibres often is effected by padding the goods with an alkaline solution of an azoic coupling component and printing with a printing paste containing diazotized ice colour diazo components either freshly prepared or in the form of stabilized diazonium salts. This is a well-known cheap process for producing azoic prints and requires no difficult treatment. However, it is open to a very serious disadvantage. The printing pastes containing the diazonium salts stabilized or unstabilized do not keep well and particularly tend to thin out rapidly losing their desired printing consistency. It is this thinning action with which the present invention is concerned.

According to the present invention the diazonium salt, either in stabilized form or freshly prepared is associated with an organic nitrogenous base soluble in aqueous mineral acids and containing at least one olefinic double bond or acetylenic triple bond.

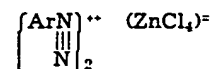
When an aromatic amine is diazotized in acid solution, a diazonium salt is formed which is generally assumed to have the following formula:



where Ar stands for the aromatic radical of the diazo component and X stands for the anion of the acid. These diazonium salts are salts of the very strong diazonium bases and the aqueous solutions contain essentially the diazonium cations and the anions of the acid used, as indicated by the formula. Some of these diazonium salts are difficult to isolate because of their great solubility. Others are not so soluble and can be easily isolated. Some are difficult to handle after isolation because of their explosiveness, others are rather stable and do not present an explosive hazard. It is also known that if the anion of the acid X⁻ is properly chosen, in almost all cases diazonium salts of lower solubility may be produced and therefore isolated, and it is also known that many of these diazonium salts have lost their explosive character and can be stored and handled in the dry state without danger; this kind of diazonium salt is sometimes referred to

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as "stabilized" diazonium salts. They comprise such compounds as certain aromatic sulphonates, without olefinic double bonds, borofluorides, and particularly salts of complex acids sometimes referred to as double salts, the most important of them being the double salts of diazonium chlorides and zinc chloride which correspond to the formula:



It should be borne in mind that also these "stabilized" diazonium salts including the above mentioned double salts are true diazonium salts, i.e. the aqueous solution contains the same diazonium cations as the solution of any other diazonium salt derived from the same base.

The present invention deals with inhibiting the thinning action of diazonium salts only and not with any similar action that might be observed with other types of diazo compounds. While it is not intended to limit the present invention to any theory of action, we believe that it is highly probable that lowering of viscosity of printing gums is essentially caused by the diazonium cation because the same kind of thing results regardless of the anion of the diazonium salt and even the double salts of the stabilized diazonium salts described above exert a similar thinning action. Presumably in aqueous solution the stabilized diazonium salts are ionized to give the same diazonium cation. The pH of the printing paste is not critical so long as it is on the acid side for the present invention does not deal with any other types of pastes. Alkaline medium, as is well known, causes rearrangement of the diazonium salts to diazo compounds of different structure.

While not desiring to limit the invention thereto, we believe that the evidence strongly indicates that the thinning action is a colloidal phenomenon rather than a chemical reaction. The following test was made:

A diazonium salt derived from 2-nitro-4-methoxy aniline was added to a printing paste made up with a starch thickener; after 20 hours the then water thin solution was coupled with an alkaline solution of betanaphthol and the azo dye formed was removed by filtration. The amount of azo dyestuff obtained indicated that the bulk of the diazonium salt was undecomposed and had reacted while the

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printing paste is valuable for the preparation of fast Bordeaux prints upon cotton cloth impregnated with arylides of 2-hydroxy-3-naphthoic acid, and is superior to a similar paste which does not contain the allyl urea because of the fact that it retains its relative viscosity and, hence, its utility for printing much better. This advantage is shown in the following table:

Printing Paste Used	Relative Viscosity Reading After 2 Min.	Relative Viscosity Reading After 2 Hours
Containing allyl urea	39.6	18.6
Without allyl urea	40.1	1.4

These relative viscosity measurements are the times in seconds for copper plated steel shot weighing approximately 0.107 gram each to fall 130 millimetres.

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Printing pastes are made in the following manner:

An amount of the zinc chloride double salt of the diazonium (or tetrazonium) chloride derived from an ice colour base equal to 0.005 equivalent part is mixed with 0.512 part of allyl guanidine sulphate and the mixture is dissolved in enough water to make 25 parts of solution. The resulting solution is intimately mixed with 75 parts of 2.5 per cent carob bean gum. These printing pastes are used for the preparation of fast colour prints upon cloth impregnated with the anilide of 2-hydroxy-3-naphthoic acid. These printing pastes retain their relative viscosity and hence their utility to the printer, very much better than similar pastes similarly prepared but without the allyl guanidine sulphate. This advantage may be seen by consulting the following table:

Base Used for Zinc Chloride Double Salt	Thinning Inhibitor in Printing Paste	Relative Viscosity Measurement After 2 Min.	Relative Viscosity Measurement After 4 Hr.	Colour of Printing on Anilide of 2-Hydroxy-3-Naphthoic Acid
2,5-dichlor aniline	Allyl guanidine sulphate	66.8	66.0	Yellowish Scarlet
"	None	61.2	10.2	"
4-nitro-2-amino anisole	Allyl guanidine sulphate	69.4	65.6	Reddish Scarlet
"	None	76.2	18.2	"
3-nitro-4-amino anisole	Allyl guanidine sulphate	85.6	40.0	Bordeaux
"	None	83.2	0.4	"
Ortho dianisidine	Allyl guanidine sulphate	66.4	49.6	Navy Blue
Ortho dianisidine	None	71.4	9.2	"

These relative viscosity measurements are the times in seconds for copper plated steel shot weighing 0.107 gram each to fall 130 millimetres.

We claim:

Claim.—1. Compositions suitable for forming printing pastes including an azoic colour forming component included in the group consisting of diazotizable amines, diazo compositions containing water soluble diazonium salts and printing pastes containing water soluble diazonium salts derived from ice colour diazo components and carbohydrate thickeners, the colour forming component having admixed therewith a compound belonging to the group consisting of organic nitrogenous bases, soluble in aqueous mineral acids, free from groups capable

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of azoic coupling or reaction with nitrous acid, and containing at least one olefinic double bond and organic nitrogenous bases, soluble in aqueous mineral acids free from groups capable of azoic coupling and free from groups capable of reaction with nitrous acid and having at least one acetylenic triple bond, and water soluble salts of the above bases with acids incapable of azoic coupling and of decomposing diazo compounds at room temperature, the amount of the nitrogenous base compound being sufficient to substantially inhibit thinning of the paste.

2. Diazo compositions containing a water soluble diazonium salt derived from an ice colour diazo component and an effective amount of a compound included in the group consisting of organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and containing at least one olefinic double bond, organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and containing at least one acetylenic triple bond, and water soluble salts of the above bases with acids incapable of azoic coupling and of decomposing diazo compounds at room temperature.

3. Printing pastes containing a carbohydrate thickener, a water soluble diazonium salt derived from an ice colour diazo component and a sufficient amount of a compound included in the group consisting of organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and containing at least one olefinic double bond, organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and containing at least one acetylenic triple bond, and water soluble salts of the above bases with acids incapable of azoic coupling and of decomposing diazo compounds at room temperature to substantially inhibit thinning of the printing thickener by the diazonium salt.

4. Diazo compositions containing a water soluble diazonium salt derived from an ice colour diazo component and an effective amount of a compound included in the group consisting of organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and containing at least one olefinic double bond and their water soluble salts with acids incapable of azoic coupling and of decomposing diazo compounds at room temperature.

5. Printing pastes containing a carbohydrate thickener, a water soluble diazonium salt derived from an ice colour diazo component and a sufficient amount of a compound included in the group consisting of organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and containing at least one olefinic double bond and their water soluble salts with acids incapable of azoic coupling and of decomposing diazo compounds at room temperature to substantially inhibit thinning of the printing thickener by the diazonium salt.

6. A composition according to claim 2 in which the diazonium salt is a diazonium chloride zinc chloride double salt.

7. A composition according to claim 4 in which the diazonium salt is a diazonium chloride zinc chloride double salt.

8. The process of stabilizing printing pastes containing a carbohydrate thickener and a diazonium salt derived from an ice colour diazo component which comprises incorporating into the paste a sufficient amount of a compound belonging to the group consisting of organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and containing at least one olefinic

double bond, organic nitrogenous bases soluble in aqueous mineral acids from groups capable of azoic coupling and containing at least one acetylenic triple bond, and water soluble salts of the above bases with acids incapable of azoic coupling and of decomposing diazo compounds at room temperature, to substantially inhibit thinning of the paste by the diazonium salt.

9. The process of stabilizing printing pastes containing a carbohydrate thickener and a diazonium salt derived from an ice colour diazo component which comprises incorporating into the paste a sufficient amount of a compound belonging to the group consisting of organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and containing at least one olefinic double bond and their water soluble salts with acids incapable of azoic coupling and of decomposing diazo compounds at room temperature, to substantially inhibit thinning of the paste by diazonium salt.

10. A process of printing fabrics containing ice colour coupling components with a printing paste containing a carbohydrate thickener, a water soluble diazonium salt derived from an ice colour diazo component, and a sufficient amount of a compound belonging to the group consisting of organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and containing at least one olefinic double bond, organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and containing at least one acetylenic triple bond, and water soluble salts of the above bases with acids incapable of azoic coupling and of decomposing diazo compounds at room temperature, to substantially inhibit thinning of the thickener by the diazonium salt.

11. A process of printing fabrics containing ice colour coupling components with a printing paste containing a carbohydrate thickener, a water soluble diazonium salt derived from an ice colour diazo component and a sufficient amount of a compound belonging to the group consisting of organic nitrogenous bases soluble in aqueous mineral acids free from groups capable of azoic coupling and contain-

ing at least one olefinic double bond and their water soluble salts with acids incapable of azoic coupling and of decomposing diazo compounds at room temperature to substantially inhibit thinning of the thickener by the diazonium salt.

12. A composition according to claim 1 in which the nitrogenous base is an allylguanidine.

13. A composition according to claim 2 in which the nitrogenous base is an allylguanidine.

14. A composition according to claim 3 in which the nitrogenous base is an allylguanidine.

15. A composition according to claim 1 in which the nitrogenous compound is tetra-allylammonium compound.

16. A composition according to claim 2 in which the nitrogenous compound is tetra-allylammonium compound.

17. A composition according to claim 3 in which the nitrogenous compound is tetra-allylammonium compound.

18. A composition according to claim 1 in which the nitrogenous compound is included in the group consisting of allylurea and beta methylallyl urea and their salts.

19. A composition according to claim 2 in which the nitrogenous compound is included in the group consisting of allylurea and beta methylallyl urea and their salts.

20. A composition according to claim 3 in which the nitrogenous compound is included in the group consisting of allylurea and beta methylallyl urea and their salts.

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